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Synthesis of Alkyl and Aryl Phosphazene High Polymers

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

New elastomers have been synthesized that contain a polyphosphazene chain and both alkyl and alkoxy side groups. In addition, new classes of polyphosphazenes have been developed that are high refractive index glasses or have second order nonlinear optical activity.

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SUMMARY OF WORK PERFORMED

During the past three years, the following progress has been made through the work of Gayanne Schrubbe-McDonnell (former graduate student, now at the du Pont Marshall Laboratories), Michael N. Mang (former graduate student, now at the Dow Laboratories in Midland, Michigan), Alexa A. Dembek (graduate research assistant), Michael L. Turner and Ian Manners (postdoctoral fellows), and Masood Parvez (postdoctoral staff crystallographer). James L. Desorcie, whose name appears on some of the publications, is a former student who graduated before the start of the grant period.

(1) New high performance elastomers have been synthesized by the polymerization of cyclic phosphazenes that bear organic side groups and halogen atoms, followed by replacement of the halogen atoms by trifluoroethoxy groups. These polymers are alternatives to the fluorophosphazene elastomers currently used in military technology and biomedicine.

(2) Detailed studies have been made of the reasons why some cyclic organophosphazenes polymerize when heated and why others do not. A new polymerization mechanism has been postulated that explains ring-ring oligomer equilibrations when all or most of the side groups are organic units, but allows polymerization when most of the side groups are halogen atoms. This work is important because of its relationship to the elastomer syntheses mentioned in item (1).

(3) Work has continued on the development of synthesis methods for the preparation of polyphosphazenes with biphenyl and related side groups linked to the phosphazene chain. A total of 42 different polymers in this series were synthesized and their solid state properties investigated. The main problem was to design and prepare polymers with two or more different side groups (to prevent crystallization and ensure transparency), while at the same time obtaining a maximum loading of pi-electron units in the side groups (to maximize the refractive index). Twenty-nine of the polymers proved to be non-crystalline. The refractive indexes (λ 632 nm) were as high as 1.686. These polymers are candidates for a number of optical engineering applications, including optical waveguides and tough, lightweight lenses.

(4) As an adjunct to the above project, a series of cyclic trimeric and tetrameric phosphazenes have been synthesized with biphenyl and related side groups, and the molecular structures have been solved by X-ray crystallography. The purpose of this work was to study side group packing and stacking in these small-molecule model compounds and to use that information to predict circumstances under which crystalline or amorphous structures might be found in the analogous high polymers.

(5) The concept of stacking and the alignment of aromatic side groups in a polyphosphazene has been extended to include systems with side groups that are capable of second-order nonlinear optical behavior. Specifically, side chains that contain an electron-donor and acceptor separated by conjugated

units such as $-C_6H_4-(C{=}C)_x-C_6H_4-$ have been linked to phosphazene ring systems and high polymers via flexible oligoethyleneoxy spacer groups. Films of the polymers have been poled and their second-order NLO activity measured. For species with $-C_6H_4\ (C{=}C)_x-C_6H_4NO_2$ units the d_{33} coefficients were near 5 pm/V. (Values above 30 pm/V have been found for related aromatic azo units.) Rapid relaxation of the side groups following cessation of poling, and locking the side groups into poled orientation, is a major challenge for future work.

PUBLICATIONS RESULTING FROM THIS WORK

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An Overview of the Current Status of Polyphosphazene Chemistry
Harry R. Allcock
Polymer Preprints 1987, 28, 437.

Report #46

The Current Status of Polyphosphazene Chemistry
Harry R. Allcock
Chapter in "Inorganic and Organometallic Polymers," (M. Zeldin, K. J. Wynne, and H. R. Allcock, eds.), ACS Symp. Ser. 1988, 250-267.

Report #47

Alkylation of Cyclic and High Polymeric Phosphazenes via Reactions Between Aluminum Alkyls and Aminophosphazenes
Harry R. Allcock, James L. Desorcie, and J. Steven Rutt
Organometallics 1988, 7, 612-619.

End-of-year report covering the period August 1, 1987 - July 15, 1988.

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Reactions of Inorganic High Polymers as a Route to Tailored Solids
Harry R. Allcock
Solid State Ionics 1989, 32/33, 761-764.

Report #49

Organometallic and Bioactive Cyclophosphazenes, and the Relationship to Inorganic Macromolecules
Harry R. Allcock
Phosphorus, Sulfur, and Silicon 1989, 41, 119-133.

Report #50

Poly(aryloxyphosphazenes) with Phenylphenoxy and Related Bulky Side Groups. Synthesis, Thermal Transition Behavior, and Optical Properties
Harry R. Allcock, Michael N. Mang, Alexa A. Dembek, and Kenneth K. Wynne
Macromolecules 1989, 22, 4179-4190.

End-of-year report covering the period June 1, 1988 - June 1, 1989.

Report #51

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Harry R. Allcock
The Chemist, January 1990, 10-16.

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Synthesis of New Polyphosphazene Elastomers
Harry R. Allcock, Gayann Schrubbe-McDonnell, and James L. Desorcie
Macromolecules 1990, 23, 3873-3877.

Report #53

A Second-Order Nonlinear Optical Poly(organophosphazene)
Alexa A. Dembek, Chulhee Kim, and Harry R. Allcock (Penn State)
Robert L. S. Devine, William H. Steier (U. Southern California)
Charles W. Spangler (Northern Illinois University)
Chemistry of Materials 1990, 2, 97-99.

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Harry R. Allcock, Gayann Schrubbe-McDonnell, and James L. Desorcie
Inorganic Chemistry 1990, 29, 3839-3844.

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End-of-year report covering the period June 1, 189 - May 31, 1990

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Alexa A. Dembek, Harry R. Allcock, Chulhee Kim (PSU), William H. Steier, Yongqiang Shi, William H. Steier (USC), and Charles W. Spangler (NIU).
ACS Symp. Ser. (in press).

Second-Order Nonlinear Optical Poly(organophosphazenes): Synthesis and Nonlinear Optical Characterization
Harry R. Allcock, Alexa A. Dembek, Chulhee Kim (PSU), Robert L. S. Devine, Yongqiang Shi, William H. Steier (USC), and Charles W. Spangler (NIU).
Macromolecules (in press).

Synthesis and Structure of Cyclic and Short Chain Linear Phosphazenes Bearing the 4-Phenylphenoxy Side Group.
Harry R. Allcock, Dennis Ngo, Masood Parvez, Robert Whittle, and William J. Birdsall (Albright College).
J. Am. Chem. Soc. (in press)

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